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The following statements are taken from the documents submitted by the applicant

- (54) Process for combinatorial preparation and testing of heterogeneous catalysts
- (57) The array of heterogeneous catalysts and/or their precursors is made from a body which preferably has parallel channels through it which contain in the at least n channels n different heterogeneous catalysts and/or their precursors, with n having the value 2, preferably 10, especially preferably 100, particularly preferably 1000, and very specially preferably 10,000. A process to produce an array comprises the following steps:
- a1) Preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,
 - a2) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions,
 - a3) simultaneous or sequential coating of the channels of the body with the solutions, emulsions and/or dispersions so that a predetermined quantity of the solutions, emulsions and/or dispersions is placed in each channel to achieve a predetermined composition, and
 - a4) if desired, heating the coated body, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C for the purpose of drying and, optionally, sintering or calcining the catalysts and/or catalyst precursors.

Description

The invention concerns a process for combinatorial preparation and testing of heterogeneous catalysts, and the catalysts obtained by this process.

"Combinatorial" chemistry was developed to produce and study new chemical compounds, as an alternative to classical chemistry, which is directed at synthesis and study of individual substances. In this process, a large number of substances are reacted in a one-pot synthesis and examined to determine whether the resulting reaction mixture has the desired properties, such as pharmacological activity. If activity is found in one such reaction mixture, then a further step is necessary to determine which specific substance in the reaction mixture was responsible for the activity. Aside from the high cost of determining the actual active compound, it has also been difficult to prevent undesired side-reactions with a large number of reactants.

In another application of combinatorial synthesis, many compounds are synthesized by controlled metering and reacting a series of reactants in a multiplicity of separate reaction vessels. In this process, it is preferably to have a single reaction product in each reaction vessel so that, for example, if there is pharmacological activity in a mixture, the starting materials used to prepare it are known immediately.

The initial applications of this more specific combinatorial synthesis were in the search for new pharmacologically active substances. More recently, the synthetic process has been extended to low-molecular-weight organic compounds and to organic and inorganic catalysts.

Preparation of organic catalysts using combinatorial processes is described in F. M. Menger et al., "Phosphatase Catalysis Developed via Combinatorial Organic Chemistry",

J. Org. Chem. 1995, 60, pages 6666 to 6667. Eight differently functionalized carboxylic acids were bound to a polyallylamine through amide bonds. Various metal ions were also bound to the polymer by complexing. The polymers obtained were then examined for their phosphatase activity. The paper does not describe how the catalysts were obtained by an automated preparation process. Only the preparation of individual catalysts is described.

C. L. Hill and R. D. Gall, "The first combinatorially prepared and evaluated inorganic catalysts. Polyoxometallates for the aerobic oxidation of the mustard analog tetrahydrothiophene (THT)", J. Mol. Catalysis A: Chemical 114 (1996), pages 103 to 111, describe combinatorial preparation and testing of polyoxometallates for aerobic oxidation of tetrahydrothiophene. The polyoxometallates were prepared by mixing different proportions of metal salt solutions of the desired metals. Tungstate, molybdate, and vanadate solutions and a sodium hydrogen phosphate solution were prepared. After measuring in the appropriate solutions, the pH was adjusted to a predetermined value and a reaction was carried out. The catalysts obtained were used in the dissolved form for the reaction. The paper does not describe whether the catalyst production was automated.

US Patent 5,449,754 describes processes for deliberate metering of different quantities of various liquid reagents into an array of reaction vessels which can, for example, resemble a spot test plate. That was done by moving the print head of an inkjet printer, connected to stock solutions

of the reactants, over the array with an X-Y positioner. The outputs of the liquids were controlled by a computer.

Infrared examination of combinatorially preparable libraries of heterogeneous catalysts is described in F. C. Moathes et al., "Infrared Thermographic Screening of Combinatorial Libraries of Heterogeneous Catalysts", *Ind. Eng. Chem. Res.* 1996, 35, 4801 to 4803. The catalysts consisted of different metallic elements supported on aluminum oxide. They were examined with respect to their catalytic activity for hydrogen oxidation. The individual catalysts were prepared by soaking aluminum oxide pellets in the corresponding metal salt solutions, drying, and calcining. The paper does not state whether the production was automated.

The different pellets were deposited on predetermined positions on a carrier and contacted with hydrogen under reaction conditions. If there was catalytic activity, the catalyst heated up, and the heating was measured with an infrared camera, so that the active catalysts could be detected.

B. E. Baker et al., "Solution-Based Assembly of Metal Surfaces by Combinatorial Methods", *J. Am. Chem. Soc.* 1996, 118, pages 8721 to 8722, describe preparation of metal surfaces of various compositions by combinatorial processes. That was done by immersing a silane-coated glass plate at a predefined rate into a colloidal gold suspension so as to produce a gradient of the gold distribution on the substrate. After the plate was removed and dried, it was rotated 90° and immersed in a solution of silver ions so as to give another concentration gradient on the plate. That produced a continuous change of the surface composition.

X.-D. Xiang et al., "A Combinatorial Approach for Materials Discovery", *Science* 268 (1995), pages 1738 to 1740, describe preparation of BiSrCaCuO and YBaCuO superconducting films on substrates. A combinatorial array of different metal compositions was produced by physical masking processes and vapor deposition techniques. After calcining, there are different compositions at the various positions in the array. They can be examined with microprobes, for example, to determine their conductivity.

WO 96/11878 describes not only preparation of such superconductor arrays but also preparation of zeolites. The required volumes of several metal salt solutions are metered, without previous mixing, with an ink jet onto a kind of spot plate, with precipitation on addition of the last solution. The preparation of BSCCO superconductors can also be accomplished by metering individual solutions of the nitrates of the required metals onto a kind of spot plate and then heating.

Different heterogeneous catalysts can be prepared by the known processes. But testing of the catalysts is expensive and often cannot be accomplished under realistic conditions, such as with the necessary residence times of the reactants at the catalysts, because the catalysts, for example, are on a large, generally flat, support and that, for example, must be provided with the gas mixture to be converted.

The object of this invention is to make available a process for preparation of arrays of inorganic heterogeneous catalysts or their precursors, in which the catalysts produced can be tested at low cost and under conditions similar to those of the industrial process. In addition, the disadvantages of the existing systems should be avoided. Also corresponding arrays should be prepared.

The objective is attained according to the invention by preparing an array of preferably inorganic catalysts and/or their precursors, built up on a body which has preferably parallel channels going through it, in which at least n channels contain n different, preferably inorganic, heterogeneous catalysts and/or their precursors, with the value of n being 2, preferably 10, especially preferably 100, particularly preferably 1000, and very especially preferably 10,000.

In one embodiment of the invention, the body is a tube bundle reactor or a heat exchanger, and the channels are tubes.

In another embodiment of the invention, the body is a block of a solid material having the channels, which are, for example, in the form of holes.

Thus the heterogeneous catalysts and/or their precursors are preferably solid contact or supported catalysts and/or their precursors. They are used as bulk catalyst, tube wall coating, or auxiliary support coating.

The term "array of inorganic heterogeneous catalysts or their precursors" means an arrangement of different inorganic heterogeneous catalysts or their precursors on predetermined, spatially separated regions of a body, preferably a body with parallel channels through it, which are preferably a tube bundle reactor or a heat exchanger. The geometric relation of the individual regions with each other can be chosen freely. For example, the regions can be arranged in the manner of a row (quasi-unidimensional), or in the manner of a checkerboard (quasi-two-dimensional). For a body with parallel channels through it, preferably a tube bundle reactor or a heat exchanger with a multiplicity of tubes parallel to each other, the arrangement becomes clear on thinking of a cross-sectional surface perpendicular to the longitudinal axes of the tubes. This is a surface in which the individual tube cross sections show the different separate regions. The regions or tubes can, for example for tubes with circular cross sections, also be closely packed, so that different rows of regions can be placed in a staggered arrangement.

The term "body" describes a three-dimensional object having a multiplicity (at least n) of channels through it. The channels connect two surface areas of the body and pass through the body. Preferably the channels are essentially, preferably completely, parallel to each other. The body can be composed of one or more materials and can be solid or hollow. It can have any suitable geometric form. Preferably it has two parallel surfaces with one opening of the channel in each surface. The channels run preferably perpendicular to these surfaces. One example of such a body is a cube or cylinder in which the channels run between two parallel surfaces. Many similar geometries are conceivable, though.

The term "channel" describes a connection running through the body between two of the openings on the surface. A channel, for instance, allows a fluid to pass through the body. The channel can have any desired geometry. It can have a cross-section which varies along the length of the channel or, preferably, a constant cross section. The channel cross section can, for instance, have an oval, circular or polygonal periphery with straight or bent connections between the corners of the polygon. Preferably all the channels in the body have the same geometry (cross section and length) and are parallel with each other.

The term "tube bundle reactor" and "heat exchanger" describe assembled parallel arrangements of a multiplicity of channels in the form of tubes, in which the tubes can have any desired cross section. The tubes are arranged in a fixed spatial relation with each other. They are preferably spatially separated from each other and are preferably surrounded by a jacket which includes all the tubes. Then, for instance, a heating or cooling medium can be passed through the jacket, so that the temperatures of all the tubes can be controlled evenly.

The term "block of a solid material" describes a body of a solid material (which in turn can be made of one or more starting materials) holding channels, in the form of holes, for example. The geometry of the channels (holes) can generally be chosen freely, as described in general above for all the channels. The channels (holes) need not be made by drilling, but can, for instance, be left open in forming the solid body/block, for example, by extrusion of an organic and/or inorganic molding material (for example, by appropriate nozzle geometry in the extrusion process). This differs from tube bundle reactors or heat exchangers in that the space in the body between the channels of the block is always filled up by the solid material. Preferably the block is made of one or more metals.

The term "predetermined" means that, for example, a row of different catalysts or catalyst precursors can be incorporated into a tube bundle reactor or heat exchanger such that the assignment of the different catalysts or catalyst precursors to the individual tubes is recorded initially and can be called up later, for example, in determination of the activity, selectivity, and/or long-term stability of the individual catalysts, so as to enable a distinct assignment of specific measurements to specific catalyst compositions. It is preferable for the preparation of the catalysts or their precursors and their distribution to the different tubes of the tube bundle reactor to be computer-controlled, such that the particular composition of a catalyst and the position of the tube in which that catalyst or catalyst precursor has been placed are stored in the computer and can be recalled later. The term "predetermined" thus distinguishes from random or statistical distribution of the generally different catalysts or catalyst precursors among the tubes of a tube bundle reactor.

Preparation of the array according to the invention, preferably of inorganic heterogeneous catalysts and/or their precursors can be accomplished by different procedures:

Process a) comprises the following steps:

- a1) Preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,
- a2) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions,
- a3) simultaneous or sequential coating of the channels of the body with the solutions, emulsions and/or dispersions so that a predetermined quantity of the solutions, emulsions and/or dispersions is placed in each channel to achieve a predetermined composition, and

- a4) if desired, heating the coated body, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C for the purpose of drying and, optionally, sintering or calcining the catalysts and/or catalyst precursors.

Process b) comprises the following steps:

- b1) Preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,
- b2) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions,
- b3) simultaneous or sequential coating of catalyst supports in the channels of the body with the solutions, emulsions and/or dispersions so that a predetermined quantity of the solutions, emulsions and/or dispersions is placed in each channel to achieve a predetermined composition, and
- b4) if desired, heating the body with the coated catalyst supports in the channels, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C for the purpose of drying and, optionally, sintering or calcining the catalysts and/or catalyst precursors.

Process c) comprises the following steps:

- c1) preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,
- c2) mixing of predetermined amounts of the solutions, emulsions, and/or dispersions and, if desired, of aids to precipitation in one or more reaction vessels operated in parallel,
- c3) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions to the mixtures obtained,
- c4) coating of one or more predetermined channels of the body with the mixture or with multiple mixtures,
- c5) repetition of steps c2) to c4) for other channels of the body until each channel has been coated with its predetermined composition of catalyst or catalyst precursor,
- c6) optional heating of the coated body, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry and optionally sinter or calcine the catalysts and/or catalyst precursors.

It preferably comprises the following steps:

- c1) preparation of solutions of compounds of elements other than oxygen which occur in the catalyst and, if desired, dispersions of inorganic support materials,
- c2) mixing of predetermined amounts of the solutions or dispersions and, if desired, of aids to precipitations in one or more reaction vessels operated in parallel with precipitation of the chemical elements that occur in the catalyst,
- c3) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions to the suspensions obtained,
- c4) coating of one or more predetermined tubes of the tube bundle reactor or heat exchanger with the suspension,
- c5) repetition of steps c2) to c4) for different tubes of the tube bundle reactor or heat exchange until the tubes have been coated with their predetermined catalyst compositions,
- c6) heating of the coated tube bundle reactor or heat exchanger, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry the catalysts and optionally to sinter or calcine them.

Process d) comprises the following steps:

- d1) preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,
- d2) mixing of predetermined amounts of the solutions, emulsions, and/or dispersions and, if desired, of aids to precipitation in one or more reaction vessels operated in parallel,
- d3) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions to the mixtures obtained,
- d4) coating of the catalyst supports in one or more predetermined channels of the body with the mixture or with one or more of the mixtures,
- d5) repetition of steps c2) to c4) for other channels of the body (as a rule, that means the ones not yet coated) until the catalyst supports (preferably all of them) in the channels have been coated with their predetermined compositions (as a rule, different from each other) of catalyst or catalyst precursor,
- d6) optional heating of the body with the coated catalyst carriers in the channels, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry the catalysts and optionally to sinter or calcine them.

In this process the adhesion of the channels (such as the inner surfaces of the tubes) of the body, or of the catalyst carrier before its coating, can be increased by chemical, physical or mechanical

pretreatment of the inner walls of the channel (such as the inside of the tube) or of the catalyst carrier or by applying an adhesive layer. This applies particularly to processes a) and c) or b) and d).

Process e comprises the following steps:

- e1) preparation of different heterogeneous catalysts and/or their precursors in the form of solid contact catalysts with predetermined compositions,
- e2) coating of each of one or more predetermined channels of the body, means having been used to prevent the heterogeneous catalysts falling out, with one or more of the heterogeneous catalysts and/or their precursors with predetermined compositions,
- e3) optional heating of the body with the heterogeneous catalysts and/or their precursors in the channels, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry the catalysts and/or catalyst precursors and optionally to sinter or calcine them.

Process f) comprises the following steps:

- f1) coating and optionally heating of predetermined catalyst carriers to produce predetermined catalyst supports of the nature defined above in processes b) or d) outside the body,
- f2) moving the catalyst carriers into predetermined channels in the body,
- f3) optional heating of the filled body, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry the catalysts and optionally to sinter or calcine them.

In this process it is preferable for the external form of the catalyst carriers to match the insides of the channels in the body, at least essentially, preferably approximately or entirely.

The invention also concerns inorganic arrays of heterogeneous catalysts which can be obtained by one or the foregoing processes. The arrays can also be prepared by an arbitrary combination of the foregoing processes.

The processes are suitable for producing a multiplicity of catalyst systems, such as are described, for example, in G. Ertl, H. Knözinger, and J. Weitkamp, Editors, "Handbook of Heterogeneous Catalysis", Wiley-VCH, Weinheim, 1997.

The invention also concerns a process g) for determining catalytic properties, especially the activity, selectivity, and/or long-term stability of the catalysts described above and in the following in a described array, comprising the following steps:

- g1) optional activation of the catalysts in the body,
- g2) controlling the temperature of the body to a desired reaction temperature,

- g3) passing a fluid reactant or a fluid reactant mixture through (one, more, or all of) the channels of the body,
- g4) removal (preferably separately) of the reacted fluids from individual channels, or from combined channels of the body,
- g5) analysis (preferably separately) of the removed reacted fluids,
- g6) optional comparative evaluation of the results of multiple analyses.

One preferred variant of the process is characterized in that, after adjusting the body temperature to a first reaction temperature in step g2), steps g3) to g6) are carried out in succession for multiple different fluid reactants or fluid reaction mixtures, after which a flushing step with a flushing gas can be introduced, and then the body temperature can be adjusted to a second reaction temperature and the reactions above can be repeated at that temperature.

At the beginning of the analysis, the combined gas stream from the entire array can be analyzed to detect whether a reaction took place at all. After that, if there was a reaction, the outputs from the individual tubes or multiple tubes can be analyzed so as to determine an optimal catalyst with a minimal number of analytical operations.

The flow can be passed through individual tubes, multiple tubes, or all the tubes together.

Preferably the fluid reactants or fluid reaction mixture are a gas or a gas mixture.

The invention allows automated preparation and catalytic testing for the purpose of mass screening of heterogeneous catalysts for chemical reactions, especially for reactions in the gas phase, and quite particularly for partial oxidations of hydrocarbons with molecular oxygen in the gas phase (gas phase oxidations).

Suitable reactions or conversions for investigation are described in G. Ertl, H. Knözinger, and J. Weitkamp, Editors, "Handbook of Heterogeneous Catalysis", Wiley-VBCH, Weinheim, 1997. This literature presents examples of suitable reactions primarily in Volumes 4 and 5, Sections 1, 2, 3, and 4.

Examples of suitable reactions include destruction of nitrogen oxides, ammonia synthesis, ammonia oxidation, oxidation of hydrogen sulfide to sulfur, oxidation of sulfur dioxide, direct synthesis of methyl chlorosilanes, oil refining, oxidative coupling of methane, methanol synthesis, hydrogenation of carbon monoxide and carbon dioxide, conversion of methanol to hydrocarbons, catalytic reforming, catalytic cracking and hydrocracking, coal gasification and liquefaction, fuel cells, heterogeneous photocatalysis, synthesis of MTBE and TAME¹, isomerizations, alkylations, aromatizations, dehydrogenations, hydrogenations, hydroformylations, selective or partial oxidations, aminations, halogenations, nucleophilic

¹ Translator's note:

MTBE: methyl tertiary butyl ether.

TAME: expansion uncertain. The usual English expansion (tosyl arginine methyl ester) is clearly inapplicable. Probable meaning: tertiary amyl methyl ether (or methyl tertiary amyl ether).

aromatic substitutions, addition and elimination reactions, oligomerizations and metatheses, polymerizations, enantioselective catalysis, and biocatalytic reactions.

The invention is explained below in more detail by use of preferred embodiments.

Preparation of the inorganic heterogeneous catalyst arrays

First, two or more, preferably 10 or more, particularly preferably 100 or more, especially 1000 or more, and very especially 10,000 or more liquid starting mixtures (called mixtures in the following) are prepared. They contain the chemical elements selected from the periodic system in the form of solutions, emulsions and/or preferably suspensions (dispersions). The mixtures prepared generally differ in their chemical compositions or concentrations. It is also possible to prepare several mixtures of the same composition to check the reproducibility.

The liquid mixtures generally contain a liquid chemical component used as a solvent, emulsifier, or dispersing agent for the other components of the mixture. Organic solvents, emulsifiers and/or water, preferably water, are used as the solvents or dispersing agents.

Aside from the chemical elements of the solvent or dispersing agent, the liquid mixtures contain one or more, preferably 2 or more, especially preferably 3 or more chemical elements, but in general they do not contain more than 50 different chemical elements at proportions greater than 1% by weight. These chemical are preferably very intimately mixed into the mixtures, for example, in the form of a mixture of various miscible solutions, intimately mixed emulsions with small droplet size and/or preferably as suspensions (dispersions) containing the chemical elements involved in the general form of a finely divided precipitate, such as in the form of a chemically mixed coprecipitate. Use of sols and gels has proved particularly good, especially use of those which contain the chemical elements involved in a largely homogeneous distribution and preferably of those which exhibit adhesion and flow behavior favorable for the subsequent coating. The initial compounds for the selected chemical elements include in principle the elements themselves, preferably in finely divided form, and further all the compounds which contain the selected chemical elements in a suitable manner, such as oxides; hydroxides; basic oxides; inorganic salts, preferably nitrates, carbonates, acetates and oxalates; organometallic compounds; alkoxides, etc. The particular starting compounds may be used in solid form, or in the form of solutions, emulsions, and/or suspensions.

Preferred elemental compounds, especially of catalytically active metals, are water-soluble oxides, hydroxides, or salts of organic or inorganic acids. Active metals appear preferably in the subgroups of the periodic system of the elements, such as in the 5th and 6th subgroups for oxidation catalysts, and in the platinum group for hydrogenation catalysts. The process according to the invention also allows screening of (atypical) elements, especially metals or metal oxides, not previously known to be active.

The liquid mixture can also contain other compounds which affect the adhesive properties and the flow behavior of the liquid mixture on the inside of the channel to be coated or on the inside of the tube, or on the catalyst carrier, and which thus influence the coating properties of the liquid mixture. Organic compounds that can be named in this connection are, for instance, ethylene glycol or glycerin, as are described in DE-A 44 42 346 or, for instance, maleic acid

copolymers. Inorganic compounds include, for example, SiO_2 , organosilicon compounds or siloxanes.

The mixtures can also contain known inorganic carriers such as Al_2O_3 , ZrO_2 , SiO_2 , Y_2O_3 , TiO_2 , activated charcoal, MgO , SiC or Si_3N_4 , which generally increase the accessible surface area of the catalytically active chemical elements in the mixture. They can also influence the catalytic properties of the active compounds obtained and can also influence the adhesive and flow characteristics of the mixtures obtained. As a rule, one obtains coatings which contain the preferred oxide, nitride, or carbide forms of the carrier material along with the actual catalytic material. However, the carrier materials named can also react with the chemical elements used to give a new solid material on the mixing of the components or on subsequent heating of the coating.

In addition, the mixtures used can also contain an organic and/or inorganic binder or binder system which stabilizes the mixture used. Suitable binders or binder systems include metal salts, metal oxides, basic metal oxides, basic metal phosphates, and/or compounds which melt eutectically at the use temperature of the catalyst.

The mixtures can also be adjusted to a defined pH range by addition of acids and/or bases. In many cases, suspensions at neutral pH are used. To do so, the mixture can advantageously be adjusted to a pH between 5 and 9, preferably between 6 and 8. Special results are obtained with the process according to the invention if the mixture has a high solids content of up to 95% by weight, preferably 50 to 80% by weight at low viscosity. If precipitation is inadequate, precipitating agents such as ammonia can be added.

In one preferred embodiment of the invention the mixture is stirred after and, in general, also during its preparation and its fluidity is measured continuously, but at least at the end of the preparation. That can be done, for example, by measuring the power consumption of the stirrer. Using this measurement, the viscosity of the suspension can be adjusted, as by adding other solvents or thickeners, so as to achieve optimal adhesion, coating thickness and coating evenness on the inner wall of the tube to be coated or on the auxiliary carrier (catalyst carrier) being coated.

The invention is essentially not limited to particular catalyst materials and catalyst compositions. The mixtures can be prepared in parallel or successively, usually in an automated manner, e. g., with the help of an automatic pipettor or pipetting robot or an ink-jet process such as is described, for example, in US Patent 5,449,754.

To coat the tubes of the tube bundle reactor or heat exchanger according to process variation a), solutions, emulsions or suspensions of individual elements or compounds of elements can be introduced into the tubes separately, simultaneously or sequentially. Simultaneous introduction can be accomplished, for example, using a modified ink-jet printhead which has separate lines for the individual solutions, emulsions, or suspensions, and which allows them to be sprayed simultaneously. Process variation b) is preferred over this process variation a). It is carried out as follows:

To prepare the catalysts or their precursors, first solutions, emulsions and/or suspensions of the elements are prepared in separate vessels. Those are often metal salt solutions, such as nitrates. The volumes of the separate solutions needed to prepare a catalyst or catalyst precursor are transferred, in the desired volume ratio, to a small separate reaction container in which the components are mixed intensely. The metering can be done with automatic pipettors or inkjets. A reaction, or precipitation of the components, can occur when the components are mixed. Precipitating agents such as ammonia can be used if desired to produce or complete precipitation, so that one often has a suspension of the mixed catalyst precursor materials.

As the suspension should have a suitable viscosity, so that it can be introduced into and distributed within a tube of the tube bundle reactor, so as to give the most even and adherent distribution of the catalyst or catalyst precursor on the inner wall of the tube, the suitable viscosity of the suspension can be adjusted to the desired value as described above using other additives. The suspension can be removed from the reaction container with pipets, for example. The suspension can be distributed in the tube, as described below, by injection or spraying. The reaction container can be completely or partially emptied in the process. Multiple reaction containers can be operated in parallel, or a single reaction container can be filled with other components, after having been partially emptied, to get a different composition.

The mixtures produced are coated in a layer 10 to 2000 μm thick on various parts of a tube reactor or heat exchange, especially a metallic one, by means of a spray process, especially on the inner walls of (preferably metallic) reaction tubes of a tube bundle reaction. In general each tube is coated with a mixture of a different composition. (It is also possible to use multiple mixtures of the same composition in multiple tubes to check the reproducibility.)

Identical catalyst compositions can also be applied to different tubes in different coating thicknesses to check on coating thickness effects (such as transport effects).

In another variation of the invention, one can use auxiliary carriers (preferably metallic or ceramic tubes) which have been coated with the liquid mixture after, or preferably before, they are inserted into the reaction tube.

The parts of the preferably metallic heat exchanger coated with the previously prepared liquid mixture are the inner walls of tubes of preferably metallic tube bundle reactors. The reaction tubes of the tube bundle reactors can have any desired cross section, but they generally have a round, especially circular, cross section. The inside diameter is preferably 0.2 to 70 mm, preferably 1 to 25 mm, and especially preferably 3 to 10 mm. The tube bundle reactor can contain up to 30,000 or more reaction tubes, preferably 10 to 20,000, and especially 100 to 10,000 reaction tubes. As a rule, each of them is coated with a mixture of different composition.

The coating with liquid mixture can be applied by sponging, slip coating, brushing, spinning, spraying and/or dipping. Also, the mixture can be poured into the individual tube and centrifuged at speeds between 200 and 1000 rpm, preferably at speeds between 300 and 800 rpm. In one preferred embodiment, the coatings on the insides of the reaction tubes are produced by spraying the liquid mixture mentioned above. The sprayed mixture material is forced into the irregularities of the substrate, preventing occurrence of air bubbles under the coating. Thus the mixture used can adhere completely to the sprayed inner surface. However, part of the mixture can be

removed by dripping out, especially if the mixture does not adhere well or if it has low viscosity. The auxiliary carriers to be coated, for instance, in the form of insides of tubes, can be completely or only partially coated. The reactor inlet and outlet in particular can be protected from being coated by a suitable means to prevent later occurrence of sealing problems when the input and output connections for the fluid are applied. Coating by spraying the mixture into the preheated tube, or applying the mixture by immersing the preheated tube, have also proven successful. That is done by preheating the metallic base structure to 60 to 500 °C, preferably 200 to 400 °C, and especially preferably to 200 to 300 °C, before spraying the suspension onto it. Then it is coated with the mixture described initially. In the process, most of the volatile components of the mixture are vaporized and a layer preferably 10 to 2000 µm thick, especially preferably 20 to 500 µm thick, of this layer of catalytically active metal oxides is formed on the preferably metallic substrate. This kind of preparation can be done, for instance, as described in DE-A-25 10 994, with the variation that the mixture is not coated on a preheated carrier but on a preheated, preferably metallic, substrate.

The coating of the reaction tube can be repeated many times in succession to produce particularly thick layers or particularly homogeneous coatings. Separate drying and/or calcining and/or sintering steps can be done between the individual coatings of a reaction tube. The inside wall coating is done, in the case of spraying, advantageously using one or more spray tubes, preferably with one or more movable spray tubes. In this process, the spray tube is moved through the tube during the spraying, for example, with an automatic system, at a defined constant or varying speed.

The thickness of the coated layer after drying and optional calcining or sintering is preferably 10 to 2000 µm, particularly preferably 20 to 500 µm.

It is also possible first to coat the inside of the tube with a coupling agent and then to coat a catalytically active cover layer containing a catalyst material on this coupling agent. The coupling agent can increase the adhesion of the catalytically active cover layer on the inside of the tube. It is also possible to increase the standing times when a coupling agent is used. Suitable coupling agents are described above.

The adhesion of the catalytic layer can also be increased by chemical, physical, or mechanical pretreatment of the inside of the tube before coating. In a chemical pretreatment, the inside of the tube can be etched with bases, for instance, or, preferably, with acids. The inside of the tube can also be roughened by blasting with a dry blasting medium, especially corundum or quartz sand, to promote adhesion. Cleaning agents which are suspensions of hard particles such as corundum in a dispersing liquid have also been used successfully.

The coating applied to the inside of the preferably metallic tube can also comprise the components of an auxiliary carrier and a catalytically active cover layer containing a catalyst material, as described, for example, in DE-A-196 00 685. In that case the auxiliary carrier preferably has an outer shape which at least essentially matches the geometry of the surface being coated. Examples of auxiliary carriers which can be considered include metallic or ceramic bodies, such as mats of wires or metal or ceramic tubes. In that case, at least the auxiliary carrier, and preferably only the auxiliary carrier, is coated with the catalytically active cover layer and the coated auxiliary carrier covers the entire inside of the reaction tube, or preferably one part of

the reaction tube. In this tube-in-tube arrangement the outer tube can, for instance, be constricted at one end to prevent the inner tubes falling out, while at the other end the excess inner tubes can be pressed into the outer tube by springs or an elastic material.

A particular feature of the process according to the invention is that each auxiliary carrier in the tube bundle reactor used generally has a different composition or a different thickness of the catalytic layer. Furthermore, the coated auxiliary carriers can easily be replaced with other auxiliary carriers with different coatings. For instance, with suitable reactor construction (provision of cutoff valves, etc.) it is possible to change individual auxiliary carriers during operation of the reactor.

When the coated tube bundle reactor is heated in vacuum or in a defined gas atmosphere to temperatures of 20 to 1500 °C, preferably 60 to 1000 °C, especially preferably 200 to 600 °C, and very especially preferably 250 to 500 °C, the solvent, preferably aqueous, is removed by drying. Also, sintering or calcining of the particles forming the coating can occur at elevated temperature. As a rule, the real catalytically active coating is obtained in this process.

The reaction tubes are preferably surrounded by a heat transfer medium, preferably a fused salt or a liquid metal such as Ga or Na, for temperature control. The liquid heat transfer medium is preferably fed into the tube bundle reactor and removed from it at opposite points, for instance, by means of a pump, so that it can be moved to a heat exchanger (e. g., an air-cooled one) for the purpose of adding or removing heat. One function of the heat transfer medium is to provide the temperature for drying, possible later sintering of the coating, and subsequent fluid phase test reaction in the reaction tubes. Another function of the heat transfer medium is to remove heat produced in the subsequent test reaction, thus preventing formation of "hot spots" along the catalyst coating, in which a higher temperature prevails locally than in the rest of the catalyst coating.

This kind of reaction control provides for the fact that heat must principally be removed during the reaction, so that practically no hot spots appear.

In another embodiment of the invention, the space between the reaction tubes is filled with a solid material, preferably a metal or a solid metal alloy. In this case, the tube bundle reactor becomes a metal block with channels or holes, as described previously. Then the inside diameter of the holes corresponds to the inside diameter of the reaction tubes of the tube bundle reactor.

It is also possible to prepare different heterogeneous catalysts with predetermined compositions in the form of 100% contact catalysts or supported catalysts by known processes, such as combinatorial processes, and to coat one or more preselected tubes of the tube bundle reactor or heat exchanger with each of the previously produced heterogeneous catalysts. Then the known types of molded pieces can be used. It is possible to vary the packed depth or the content of inert material in a packing, or to adjust other packing parameters, for each individual tube.

The catalysts are tested by reacting fluid reactants or reaction mixtures, which are as a rule liquid or, preferably, gaseous. It is preferred to test oxidation catalysts by parallel or successive introduction of a gas mixture to individual, multiple, or all tubes of the coated tube bundle reactor. The gas mixture comprises a mixture of one or more saturated, unsaturated, or multiply

unsaturated organic starting materials (such as hydrocarbons, alcohols, aldehydes, etc.), oxygen-containing gases (such as air, O_2 , N_2O , NO , NO_2 , or O_3) and/or, for instance, H_2 , and optionally an inert gas such as nitrogen or a noble gas, at temperatures of 20 to 1200 °C, preferably 50 to 800 °C, especially preferably 80 to 600 °C. Parallel or successive separate removal of the individual gas streams from the individual, multiple, or all tubes of the tube bundle reactor is provided by a suitable means.

The reaction tubes of the tube bundle reactor, which are, as a rule, differently coated, are, for instance, fed a gas mixture comprising, for example, an oxygen-containing gas (e. g., air, O_2 , N_2O , NO , NO_2 , O_3) and/or H_2 and the organic material to be converted (such as propene or o-xylene). Aside from the gaseous materials listed, other gaseous materials, such as materials containing chlorine or phosphorus, may also be present. The gas mixture can be directed to the individual reactor tubes in succession. In the preferred embodiment, the gas mixture is passed through the reaction tubes in such a manner that the gas mixture passes through all the tubes simultaneously. During the buildup of the reaction, that is, during the activation time of the catalytic coatings, the feed compositions, the temperature of the heat exchange medium or of the reaction tubes, the residence time of the feed, and/or the total pressure of the gas in the tube bundle reactor can be changed. The gases leaving the reaction tubes, produced by conversion of the ingoing reaction gases, are in general removed separately, but can also be removed together, and are analyzed for their composition, for instance, by various samples or various analytical procedures.

The gas mixtures listed can also be fed to the coated tube bundle reactors immediately after coating with the suspension (omitting drying and sintering or calcining). In that case, the drying and any subsequent sintering process occur in the given gas mixture. That can change the composition of the coating inside the tube. Particularly under strongly reducing conditions, oxide coatings can lose part of all of their oxygen. Under strongly oxidizing conditions, they can absorb oxygen in their structure.

Feeding of a constant gas mixture to the individual, differently coated, reaction tubes of the tube bundle reactor can, for instance, be done through a gas supply hood which can be placed essentially gas-tight on the tube bundle reactor.

The gases used can be mixed before they are introduced into the gas supply hood, or only in it, as by means of a static mixer.

The individual reaction gases can be removed through an essentially gas-tight means placed on the tube bundle reactor, so that the individual reaction gases are taken off separately from the individual, multiple, or all the reaction tubes and separately analyzed by means of a valving system.

Another way of removing the individual gases from the individual, generally differently coated reactor tubes consists of, for instance, a mechanically moved, computer-controlled "sniffer system" with a sniffing line for the gas to be removed which is positioned essentially automatically on, in, or above the output of the individual reactor tube and then collects a sample of the reaction gas. The positioning and removal of the particular reaction gas is preferably done so that only the actual reaction gas to be analyzed later gets into the sniffer system, and not any

extra foreign outside gas. If the sniffer system is positioned on the end of the reaction tube, it is advantageous to make an essentially gas-tight application of the sniffer system to the end of the reactor tube, as by pressing the sniffer system onto the end of the reactor tube. If the sniffer system is positioned in or above the output of the particular reaction tube, then it is desirable to draw the reaction gases in by means of reduced pressure in the sniffer line, such that the volume of reaction gases drawn in is limited so that no other foreign gases are drawn into the sniffer line. In the case in which the sniffer line is positioned in the output of the particular reaction tube, it has proved particularly advantageous for the end of the sniffer tube to be constricted so that inserting the end of the sniffer line into the end of the particular reaction tube assures

that the reaction gases flowing out of the particular reaction tube are sealed off essentially gas-tight from the surrounding volume. After completion of collection of the reaction gas from the particular reaction tube of the tube bundle reactor, the sniffer system is positioned, preferably automatically, in, on, or above another reaction tube so as to accomplish the next gas collection there. This tube is as a rule the nearest output of another reaction tube. In this way, all the output gases from the reaction tubes can be sampled separately and then analyzed. It is not only possible for the sniffer line to be positioned on, on, or above the output of the reaction tube with the tube bundle reactor fixed. Alternately, the sniffer system can remain fixed with the tube bundle reactor moved appropriately. During positioning, it is also for both the sniffer system and the tube bundle reactor to be moved. With one preferred process variable the tube bundle reactor remains unchanged and only the sniffer system is moved above or onto the individual tube ends during positioning. With another preferred process variable the tube bundle reactor is rotated about its axis during positioning, while the sniffer line is moved linearly toward the axis of rotation of the tube bundle reactor and, in positioning on the particular reaction tube ends, the sniffer system is also moved parallel to the reactor axis.

It is also possible to use several sniffer systems simultaneously to sample the different reaction gases. Also, samples can be collected from multiple combined tubes.

As an alternative to the gas supply hood, the gas feed line can also [be moved] by a principle similar to collecting the gases through the "sniffer lines", so that the individual tubes are tested separately. Of course, the output gas sniffer line must be positioned synchronously with the input gas feed line.

Screening of the catalytic performances of the individual catalytic coatings of the individual reaction tubes can be accomplished by chemical analysis of the individual gas streams using suitable methods which are themselves known. The gas streams collected from the individual reaction tubes of the tube bundle reactor are analyzed separately using, for example, suitable equipment, for example, gas chromatography with FID and/or WLD² or, for example by mass spectrometry. The gas composition obtained is analyzed for its relative content of the desired product or of various desired products, and the concentrations are related to the amounts of reactants converted so as to yield values for the individual conversions (activity) and the product selectivities. In many cases it is useful to measure the product selectivities of the individual

² Translator's note:

FID: Flame ionization detector.

WLD: expansion unknown; some other gas chromatographic detector.

catalysts over a long period of generally hours to several weeks. In selection of the most suitable catalytic coating for the particular reaction, it may be useful, to limit the number of gas analyses, to make repeat measurements only of the gas compositions of selected reactor tubes which exceed a desired limiting concentration or limiting selectivity for certain products.

After the catalytic test, the inner catalytic layers which were applied can be removed so that the tube bundle reactor is again usable for a new catalytic coating.

The catalytic coatings can be renewed by removing, at least essentially, the old catalytically active cover layer of the coating and applying a new catalytically active coating by sponging, brushing, spinning, spraying and/or dipping. It is convenient to select the same coating process with which the catalytic coating just removed was applied. Removal of the old catalytically active cover layer can be accomplished in a simple manner particularly by blasting with a blasting medium such as corundum, silicon carbide, fine sand or the like. Alternatively, steam treatment or use of chemical removal methods have proven effective.

One efficient method for removing the internal coatings—for instance, after catalyst testing—is use of brushing systems, similar to bottle brushes, usually in combination with the cleaning agents described. It is preferred to remove the inside coatings in a manner which is as automated as possible.

The process according to the invention can easily be carried out in an automated form by robots. Coating of tubes with the catalyst assures optional fluid flow, causes only slight pressure loss, and prevents plugging of the individual reaction tubes of the tube bundle reactor.

The spatial separation and the unequivocal assignment of the tested coatings offers the advantage of being able to test a number of materials, generally matching the number of tubes, in parallel with reduced time and cost with one piece of equipment (tube bundle).

In comparison with other systems, such as perforated plates, CVD³ arrays, and the like, the tube bundle reactor offers the advantage of performing the testing as nearly as possible like an industrial process (scale-up capability is retained). Industrially relevant optimization can be done very rapidly and economically, particularly because many catalysts can be tested in parallel/simultaneously under the same conditions.

³ Translator's note:

CVD: not identified, but very probably "chemically vapor-deposited".

Claims

1. Array of heterogeneous catalysts and/or their precursors, comprising a body having preferably parallel channels through it and which contains at least n different heterocyclic catalysts and/or their precursors in its at least n channels, with n having the value of 2, preferably 10, particularly preferably 100, very particularly 1000 and especially preferably 10,000.
2. Array according to Claim 1, characterized in that the heterogeneous catalysts are inorganic heterogeneous catalysts.
3. Array according to Claim 1 or Claim 2, characterized in that the body is a tube bundle reactor or heat exchanger and that the channels are tubes, or the body is a block of a solid material which has the channels.
4. Array according to one of Claims 1 to 3, characterized in that the heterogeneous catalysts and/or their precursors are solid catalysts or catalysts on supports and/or their precursors and are present as bulk catalyst, tube wall coating or coating on auxiliary supports.
5. Process for preparing arrays according to one of Claims 1 to 4, comprising the following steps:
 - a1) Preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,
 - a2) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions,
 - a3) simultaneous or sequential coating of the channels of the body with the solutions, emulsions and/or dispersions so that a predetermined quantity of the solutions, emulsions and/or dispersions is placed in each channel to achieve a predetermined composition, and
 - a4) if desired, heating the coated body, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C for the purpose of drying and, optionally, sintering or calcining the catalysts and/or catalyst precursors.
6. Process for preparing arrays according to one of Claims 1 to 4, comprising the following steps:
 - b1) Preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,

- b2) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions,
 - b3) simultaneous or sequential coating of the channels of the body with the solutions, emulsions and/or dispersions so that a predetermined quantity of the solutions, emulsions and/or dispersions is placed in each channel to achieve a predetermined composition, and
 - b4) if desired, heating the body with the coated catalyst supports in the channels, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C for the purpose of drying and, optionally, sintering or calcining the catalysts and/or catalyst precursors.
7. Process for preparing arrays according to one of Claims 1 to 4, comprising the following steps:
- c1) preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,
 - c2) mixing of predetermined amounts of the solutions, emulsions, and/or dispersions and, if desired, of aids to precipitation in one or more reaction vessels operated in parallel,
 - c3) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions to the mixtures obtained,
 - c4) coating of one or more predetermined channels of the body with the mixture or with multiple mixtures,
 - c5) repetition of steps c2) to c4) for other channels of the body until each channel has been coated with its predetermined composition of catalyst or catalyst precursor.
 - c6) optional heating of the coated tube bundle reactor or heat exchanger, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry the catalysts and optionally to sinter or calcine them.
8. Process for preparing arrays according to one of the Claims 1 to 4, comprising the following steps:
- d1) preparation of solutions, emulsions and/or dispersions of elements and/or compounds of elements in the catalyst and/or catalyst precursors and, if desired, dispersions of inorganic support materials,

- d2) mixing of predetermined amounts of the solutions, emulsions, and/or dispersions and, if desired, of aids to precipitation in one or more reaction vessels operated in parallel,
 - d3) if desired, addition of coupling agents, binders, viscosity controllers, pH-control agents and/or solid inorganic supports in the solutions, emulsions and/or dispersions to the mixture(s) obtained,
 - d4) coating of one or more predetermined channels of the body with the mixture or with one or more of the mixtures,
 - d5) repetition of steps c2) to c4) for other channels of the body until the catalyst supports in the channels have been coated with their predetermined compositions of catalyst or catalyst precursor,
 - d6) optional heating of the body with the coated catalyst carriers in the channels, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry the catalysts and optionally to sinter or calcine them.
9. Process according to Claim 5 or Claim 7, characterized in that the adhesive nature of the channels of the body is increased before the coating by chemical, physical or mechanical pretreatment of the inner walls of the channels or by applying an adhesive layer.
10. Process for preparing arrays according to one of Claims 1 to 4, comprising the following steps:
- e1) preparation of different heterogeneous catalysts and/or their precursors in the form of solid contact catalysts with predetermined compositions.
 - e2) coating of each of one or more predetermined channels of the body, means having been used to prevent the heterogeneous catalysts falling out, with one or more of the heterogeneous catalysts and/or their precursors with predetermined compositions,
 - e3) optional heating of the body with the heterogeneous catalysts and/or their precursors in the channels, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry the catalysts and/or catalyst precursors and optionally to sinter or calcine them.
11. Process for preparing arrays according to one of Claims 1 to 4, comprising the following steps:
- f1) coating and optionally heating of predetermined catalyst supports to produce predetermined supported catalysts of the nature defined above in processes b) or d) outside the body
 - f2) moving the catalyst carriers into predetermined channels in the body

- f3) optional heating of the filled body, optionally in the presence of inert or reactive gases, to a temperature in the range of 20 to 1500 °C to dry the catalysts and optionally to sinter or calcine them.
- 12. Process according to Claim 11, characterized in that the outer shape of the supported catalysts at least essentially matches the inside shape of the channels in the body.
- 13. Array, obtainable by a process according to one of Claims 5 to 12.
- 14. Process for determining the activity, selectivity and/or long-term stability of the catalysts in an array according to one of the claims 1 to 4 or 13, comprising the following steps:
 - g1) optional activation of the catalysts in the body
 - g2) control of the body temperature to a desired conversion temperature
 - g3) passing a fluid reactant or a mixture of fluid reactants through channels in the body
 - g4) removal of the converted fluids from individual or combined channels of the body
 - g5) analysis of the removed converted fluids
 - g6) optional comparative evaluation of the results of multiple analyses.
- 15. Process according to Claim 14, characterized in that, after controlling the body temperature at a first conversion temperature in step g2), the steps g3) to g6) are carried out in succession for multiple different fluid reactants or fluid reaction mixtures after which a flushing step with a flushing gas can be introduced, and then the body can be adjusted to a second conversion temperature and the reactions above can be repeated at that temperature.
- 16. Process according to Claim 14 or 15, characterized in that the fluid reactant or the fluid reaction mixture is a gas or a gas mixture.
- 17. Process according to one of Claims 14 to 16, characterized in that the reaction is a gas-phase oxidation.
- 18. Process according to Claim 17, characterized in that a reaction mixture containing molecular oxygen is used.
- 19. Process according to Claim 6 or Claim 8, characterized in that the ability of the catalyst support to adhere to the body is increased before the coating by chemical, physical or mechanical pretreatment of the catalyst support or by applying an adhesive layer.
- 20. Process according to one of Claims 5 to 12 and 14 to 19, characterized in that the process is automated.

